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(54) VINYL POLYMER HAVING FUNCTIONAL GROUPS AT ENDS, METHOD FOR MANUFACTURING THE SAME, AND CURABLE COMPOSITION CONTAINING THE VINYL POLYMER HAVING FUNCTIONAL GROUPS AT ENDS

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a vinyl polymer having functional groups at its ends, in which physical properties such as elongation and tensile strength attributable to chain extension are well balanced with durability such as resistance to heat and water attributable to a network structure and, furthermore, in which resins different in composition are coupled into an AB-type block polymer usable for the manufacture of a viscous adhesive, sealer, elastic adhesive, paint, foam, film, thermoplastic elastomer, damping material, various molding materials, resin modifier or the like; a method for manufacturing the same; and a curable composition containing a vinyl polymer having functional groups at its ends.

$$X - R^A - N(R^A) - P - (G, R^A, R^A, R^A) - P - N(R^A) - R^A - X \quad (1)$$

SOLUTION: The vinyl polymer having functional groups at its ends, the method for manufacturing the same, and the curable composition containing the vinyl polymer having functional groups at its ends involve formula (1), where X is -OH, -COOH, a silyl group, an alkenyl group, or an aryl group and P is a vinyl polymer whose ends connect to the end groups X through the intermediary of amine groups, etc., on both sides.

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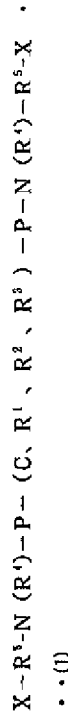
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CLAIMS

[Claim(s)]

[Claim 1] A vinyl system polymer which has a functional group at the end expressed with a following general formula (1):

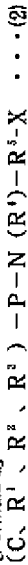
[Formula 1]



[X express the basis of either a hydroxyl group, $\text{-NR}^6\text{R}^7$, a carboxyl group, a silyl group, a vinyl group, an alkenyl group or an aryl group among a formula, and P, Express independent or the copolymer of the vinyl system monomer in which a radical polymerization is possible, and (C, R¹, R², R³). In one side and the carbon atom of a polymer component or a copolymer component which are expressed with P, it joins together. Mean that P of another side has combined with either the above-mentioned carbon atom or R¹, R² and R³, and R¹, R², and R³. Respectively Hydrogen, halogen, the alkyl group of the carbon numbers 1-20, the cycloalkyl group of the carbon numbers 3-8, C(=Y) NR⁶R⁷, C(=Y) R⁸, a carboxylic acid chloride group, A hydroxyl group, a cyano radical, the alkenyl group of the carbon numbers 2-20, the alkynyl group of the carbon numbers 2-20, A oxilanyl group, a glycidyl group, an allyl group, an aryl group, a -Ar-mold, -(Ar-R)-mold aromatic ring, or -(R-Ar-R)-mold aromatic ring. (However, the aromatic ring in which Ar has an aromatic ring or one or more substituents, and R express an aliphatic group), a heterocyclyl group, an aralkyl group, an ARARUKENIRU group. The alkyl group of the carbon numbers 1-6 which until all replaced by the halogen atom from one of the hydrogen atom. And although either the alkyl group of the carbon numbers 1-6 replaced by 1 to three bases chosen from the group of the alkoxy group of the carbon numbers 1-4, an aryl group, a heterocyclyl group, C(=Y) NR⁶R⁷, and C(=Y) R⁸, an OKIRANIRU group or a glycidyl group is expressed. It is two or less pieces that both R¹, R², and R³ can take hydrogen. R⁴ expresses hydrogen, the alkyl group of the carbon numbers 1-6, the alkenyl group of the carbon numbers 1-6, an aryl group, a phenyl group, or benzyl, and R⁵. Either of the alkyl groups of the carbon numbers 1-20 containing one or more the polar groups or aromatic rings which were chosen from the group which consists of an ester group, an amide group, an amino group, a urethane group, a sulfinyl group, a vinyl group, and the benzene ring into the alkyl group of the carbon numbers 1-20, its main chain, or a side chain is expressed. Y is NR⁹ or an oxygen atom, and NR⁶R⁷. The alkyl group of the carbon numbers 1-5 or the cycloalkyl group of the carbon numbers 1-5 which both R⁶ and R⁷ combined with the nitrogen atom. Or R⁶ and R⁷ join together, and the alkylene group of the carbon numbers 2-5 is formed. The thing in which the annular group of 3 which forms a nitrogen atom and the annular group of 3-6 member, or has a side chain-6 members was formed is expressed, R⁸ is an alkyl group of the carbon numbers 1-20, an alkoxy group of the carbon numbers 1-20, an aryloxy group, or a heterocyclyl oxy group, and R⁹ expresses the alkyl group or aryl group of hydrogen, a straight chain, or the carbon numbers 1-20 of branching.]

[Claim 2] A vinyl system polymer which has a functional group at the end expressed with a following general formula (2).

[Formula 2]



[Each of X, P and R¹ - R⁵ is the same as that of the contents of the agreement in a general formula (1) among a formula, and (C, R¹, R², R³) mean having joined together in the polymer component or copolymer component expressed with P and a carbon atom.]

[Claim 3] A vinyl system polymer which has a functional group at the end expressed with a following general formula (3).

$$[\text{Formula 3}]$$

$$(C, R^1, R^2, R^3) - [P-N(R^4)-R^5-X], \dots (3)$$

[Each of X, P and $R^1 - R^5$ is the same as that of the contents of the agreement in a general formula (1) among a formula, and Z. Are an integer of 3-6 and (C, R^1 , R^2 , R^3)-[P-N(R^4)- R^5 -X]_Z, it means that, joined together in at least one and a carbon atom among the polymer components or copolymer components which are expressed with Z P, and either a carbon atom, R^1 , R^2 and R^3 have combined the remaining P.]

[Claim 4] In a vinyl system polymer which has a functional group at the end expressed with the general formula (1) according to claim 1, (C, R¹, R², R³) CHR¹⁰-Ar-CHR¹¹, CHR¹⁰-(Ar-R)-CHR¹¹ or CHR¹⁰-(R-Ar-R)-CHR¹¹ (Ar among a formula) An aromatic ring and R which have an aromatic ring or one or more substituents express an aliphatic group, and R¹⁰ and R¹¹ express an alkyl group or an aryl group of straight chain shape of the carbon numbers 1-20, or branching respectively. A vinyl system polymer which has a functional group at the end according to claim 1 with which it is expressed.

[Claim 5] In a vinyl system polymer which has a functional group at the end expressed with the general formula (2) according to claim 2, $(C, R^1, R^2, R^3) - Ar-CHR^{10}, (Ar-R)-CHR^{10}$, or $(R-Ar-R)-CHR^{10}$ (Ar: among a formula) An aromatic ring and R^{10} which have an aromatic ring or one or more substituents express an alkyl group or an aryl group of straight chain shape of the carbon numbers 1-20, or branching. A vinyl system polymer which has a functional group at the end according to claim 2 with which it is expressed.

[Claim 6] In a vinyl system polymer which has a functional group at the end expressed with the general formula (3) according to claim 3, $(C, R^1, R^2, R^3)-Ar-(CHR^{10})-(CHR^{11}) \dots (CHR^{10+z-2})-(CHR^{10+z-1})-(Ar-R)-(CHR^{10})-(CHR^{11}) \dots (CHR^{10+z-2})-(CHR^{10+z-1})$ or $-(R-Ar-R)-(CHR^{10})-(CHR^{11}) \dots (CHR^{10+z-2})-(CHR^{10+z-1})$ [As for an aromatic ring in which Ar has an aromatic ring or one or more substituents, and Z, an integer of 3-6, $R^{10}, R^{11}, \dots, R^{10+z-2}$, and R^{10+z-1} express an alkyl group or an aryl group of straight chain shape of the carbon numbers 1-20, or branching respectively among a formula. A vinyl system polymer which has a functional group at the end according to claim 3 expressed with 1.

[Claim 7] That acrylic ester (meta) of a copolymer is independent or an independent or vinyl system polymer of a vinyl system monomer in which a radical polymerization is possible which has a functional group at the end which is a copolymer shown by P in a general formula which expresses with claims 1-5 or an end given in 6 a vinyl system polymer which has a functional group.

[Claim 8] That acrylonitrile (meta) of a copolymer is independent or an independent or vinyl system polymer of a vinyl system monomer in which a radical polymerization is possible which has a functional group at the end which is a copolymer shown by P in a general formula which expresses with claims 1-5 or an end given in 6 a vinyl system polymer which has a functional group.

[Claim 9] A vinyl system polymer which has a functional group at claims 1-7 whose number average molecular weights are 500-50000, and whose end functional group introduction rates are not less than 90% or the end given in 8.

[Claim 10] It is a manufacturing method of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9. A vinyl system monomer is polymerized and ranked second, using an iodine content compound which contains intramolecular at least one iodine atoms combined with a carbon atom of a side chain of an aromatic ring as a chain transfer agent. It is general formula NH

(R⁴)-R⁵-X (X, R⁴, and R⁵ among a formula) to an obtained polymer. All are the same as that of the contents of the agreement in a general formula (1). A manufacturing method of a vinyl system polymer which has a functional group at the end making an amine compound expressed react and introducing a functional group into a molecular terminal.

[Claim 11] A hardenability constituent which becomes considering a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 as the main ingredients.

[Claim 12] A hardenability constituent containing a compound which contains a functional group of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9, and the above-mentioned end, and a functional group in which a reaction is possible in [two or more] a molecule.

[Claim 13] A functional group of an end of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 is a hydroxyl group. The hardenability constituent according to claim 12 in which a compound which contains a functional group in which this and a reaction are possible in [two or more] a molecule contains at least one sort of compounds chosen from a group of a polyfunctional isocyanate compound, melamine resin, and urea resin.

[Claim 14] A functional group of an end of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 is a carboxyl group. The hardenability constituent according to claim 12 in which a compound which contains a functional group in which this and a reaction are possible in [two or more] a molecule contains at least one sort of compounds chosen from a group of a polyfunctional isocyanate compound, a polyfunctional epoxy compound, and a polyfunctional aziridine compound.

[Claim 15] A functional group of an end of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 is a silyl group. The hardenability constituent according to claim 12 in which a compound which contains a functional group in which this and a reaction are possible in [two or more] a molecule contains at least one sort of compounds chosen from a group of a multivalent hydrosilyl compound, a multivalent hydrogen silicone compound, a multivalent alkoxysilyl compound, and silica.

[Claim 16] A hardenability constituent which a functional group of an end of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 is a vinyl group, and contains this and a vinyl system monomer which contains at least one polymerization nature unsaturation group in intramolecular.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the hardenability constituent containing the vinyl system polymer which has a functional group at the vinyl system polymer which has a functional group at the end, its manufacturing method, and said end.

[0002]

[Description of the Prior Art]A bridge is constructed by using combining a hardening agent independent [the polymer which has a functional group at the end], or suitable, and giving the hardened material which was excellent in heat resistance, a water resisting property, other endurance, etc. is known.

[0003]Since the chain extension not only by reticulated-izing by bridge construction but bridge construction of ends happens efficiently as compared with the polymer which has a functional group inside a molecule when it has a functional group in the both ends of the above-mentioned polymer, the amount of polymers by which chain extension was carried out to straight chain shape can be formed, and resin excellent in elongation or tensile strength is obtained. Formation of the network structure by chain extension takes place easily by having a functional group at the end also in star shape polymer. It can control that crosslinking density becomes superfluous and resin of outstanding physical properties is obtained. About the polymer which has a functional group in one end, by the function as the resin modifier using the functional group of the end, or a surface-active agent, and different coupling of the resin of a presentation, the so-called block polymer of an AB type can be compounded, and the practical use as a resin modifier and a compatibilizer is expected similarly.

[0004]About the rubber system polymer which has a functional group at the end, composition (Society of Rubber Industry, Japan.) of the telechelic polybutadiene composition by many living polymerization methods is made by the present, and according to living anionic polymerization The composition (JP.3-287613A) of polychloroprene etc. which have a hydroxyl group in the both ends by the infirter method are reported in the 48th volume, No. 5, the 263rd page, and 1975.

[0005]Polymer of a both-ends hydroxyl group like a polypropylene glycol is also used as the raw material of urethane application or a sealing material, and a modifier of epoxy adhesive. Polyethylene terephthalate and polyester resin like polycaprolactone are also used abundantly at the use of the same kind etc.

[0006]However, especially (meta) about polar high vinyl system monomers other than the above containing acrylic ester and acrylonitrile (meta), the manufacturing method with a vinyl system polymer effective in an end which has a functional group using the high radical polymerization method of flexibility is in the actual condition which is not yet put in practical use.

[0007]As a polymer which introduced the functional group into the end, for example to JP.5-255415.A. The synthesizing method of the acrylic polymer which has an alkenyl group in both ends (meta) is indicated using alkenyl group content disulfide as a chain transfer agent. The acrylic polymer which has a hydroxyl group in both ends at JP.5-262808.A using the disulfide which has a hydroxyl group is compounded, further, the hydroxyl group of an end is used and the synthesizing method of the acrylic polymer which has an alkenyl group at the end (meta) is indicated.

[0008]However, in the method indicated by JP.5-255415.A. In the method which was not easy for introducing a functional group into both ends certainly, and was indicated by JP.5-262808.A. In order to introduce a hydroxyl group into an end and certainly, a lot of chain transfer agents must be used, it

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leaves a manufacturing process top problem, and the manufacturing method with effective all cannot be good.

[0009]In recent years, research of living polymerization methods, such as living ionic polymerization and living radical polymerization, is done briskly. Control of a molecular weight and molecular weight distribution is possible for the polymer obtained by these living polymerization methods, and manufacture of the polymer which has a functional group at the end can perform it comparatively easily by changing the active group of a living end into arbitrary substituents. For example, the synthetic method of the acrylic acid macro monomer which has a functional group at the end by anionic polymerization (meta) is indicated by the Patent Publication Heisei No. 501883 [four to] gazette.

[0010]However, in order that in the case of anionic polymerization control of a termination reaction or a chain transfer reaction cannot be performed and a reaction may not progress in living, if it is neither an antiposic requirement nor a low temperature service as indicated by the above-mentioned gazette, it becomes difficult to change the active group of an end into arbitrary substituents, and it has the problem of being what lacks in practicality.

[0011]On the other hand, in living radical polymerization, compared with ionic polymerization, the predominance attracts attention to reaction controllability from viewpoints of the looseness of the reaction condition of what is a little inferior, the simple nature of operation, etc. For example, the manufacturing method of the acrylic polymer which has an alkenyl group at the end which used the organic sulfonyl halide compound as the initiator, and made the metal complex the catalyst (meta) is indicated by JP.9-272714.A. However, when a metal complex is made into a catalyst like the method indicated by the above-mentioned gazette, washing of the metal in the refining processes of resin is difficult, and is not practical.

[0012]

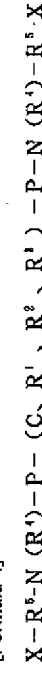
[Problem(s) to be Solved by the Invention]This invention was made in view of the above-mentioned fact, and is ***, the purpose by making into block polymer of an AB type the resin of a presentation which is given with sufficient balance of physical properties boiled and depended, such as elongation and tensile strength, and endurance by reticulated-izing, such as heat resistance and a water resisting property, and is different by coupling. An adhesive, a sealing agent, elastic adhesives, a paint, foam, a film, thermoplastic elastomer, It is providing the hardenability constituent containing the vinyl system polymer which has a functional group at the vinyl system polymer which has a functional group at the end with which extensive uses, such as a sound deadener, various molding materials, and a resin modifier, can be presented, its manufacturing method, and said end.

[0013]

[Means for Solving the Problem]A vinyl system polymer which has a functional group at the end of the invention according to claim 1 is expressed with a following general formula (1).

[0014]

[Formula 4]



• • (1)

[0015]X express the basis of either a hydroxyl group, $-NR^6R^7$, a carboxyl group, a silyl group, a vinyl group, an alkenyl group or an allyl group among a formula, and P, Express independent or the copolymer of the vinyl system monomer in which a radical polymerization is possible, and (C, R^1, R^2, R^3) . In one side and the carbon atom of a polymer component or a copolymer component which are expressed with P, it joins together, Mean that P of another side has combined with either the above-mentioned carbon atom or R^1, R^2 and R^3 , and R^1, R^2 and R^3 . Respectively Hydrogen, halogen, the alkyl group of the carbon numbers 1-20, the cycloalkyl group of the carbon numbers 3-8, $C(=Y)$ NR^6R^7 , $C(=Y) R^8$, a carboxylic acid chloride group, A hydroxyl group, a cyano radical, the alkenyl group of the carbon numbers 2-20, the alkenyl group of the carbon numbers 2-20, A oxilanyl group, a glycidyl group, an allyl group, an aryl group, a $-Ar$ -mold, $-(Ar-R)$ -mold aromatic ring, or $-(R-Ar-R)$ -mold aromatic ring. (However, the aromatic ring in which Ar has an aromatic ring or one or more

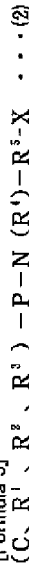
http://www4.ipdl.inpit.go.jp/cgi-bin/tran_web.cgi?ejie?atw_u=http%3A%2F%2Fwww4.ipdl... 2010/03/03

substituents, and R express an aliphatic group, a heterocyclic group, an aralkyl group, an ARARUKENIRU group. The alkyl group of the carbon numbers 1-6 which until all replaced by the halogen atom from one of the hydrogen atom. And although either the alkyl group of the carbon numbers 1-6 replaced by 1 to three bases chosen from the group of the alkoxy group of the carbon numbers 1-4, an aryl group, a heterocyclic group, $C(=Y)NR^6R^7$, and $C(=Y)R^8$, an OKIRANIRU group or a glycidyl group is expressed. It is two or less pieces that both R^1 , R^2 , and R^3 can take hydrogen. [0016] R^4 expresses hydrogen, an alkyl group of the carbon numbers 1-6, an alkenyl group of the carbon numbers 1-6, an aryl group, a phenyl group, or benzyl, and R^5 . Either of the alkyl groups of the carbon numbers 1-20 containing one or more polar groups or aromatic rings which were chosen from a group which consists of an ester group, an amide group, an amino group, a urethane group, a sulfinyl group, a vinyl group, and the benzene ring into an alkyl group of the carbon numbers 1-20, its main chain, or a side chain is expressed. Y is NR^6 or an oxygen atom, and NR^6R^7 . An alkyl group of the carbon numbers 1-5 or a cycloalkyl group of the carbon numbers 1-5 which both R^6 and R^7 combined with a nitrogen atom. Or R^6 and R^7 join together, and an alkylene group of the carbon numbers 2-5 is formed. A thing in which an annular group of 3 which forms a nitrogen atom and an annular group of 3-6 member, or has a side chain - 6 members was formed is expressed. R^8 is an alkyl group of the carbon numbers 1-20, an alkoxy group of the carbon numbers 1-20, an aryloxy group, or a heterocyclic oxy group, and R^9 expresses an alkyl group or an aryl group of hydrogen, a straight chain, or the carbon numbers 1-20 of branching.]

[0017] A vinyl system polymer which has a functional group at the end of the invention according to claim 2 is expressed with a following general formula (2).

[0018]

[Formula 5]

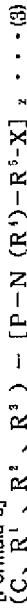


[0019] [Each of X, P and $R^1 - R^5$ is the same as that of the contents of the agreement in a general formula (1) among a formula, and (C, R^1, R^2, R^3) mean having joined together in the polymer component or copolymer component expressed with P, and a carbon atom.]

[0020] The vinyl system polymer which has a functional group at the end of the invention according to claim 3 is expressed with a following general formula (3).

[0021]

[Formula 6]



[0022] [Each of X, P and $R^1 - R^5$ is the same as that of the contents of the agreement in a general formula (1) among a formula, and Z, Are an integer of 3-6 and $(C, R^1, R^2, R^3) - [P - N(R^4) - R^5 - X]_z$. It means that joined together in at least one and a carbon atom among the polymer components or copolymer components which are expressed with Z P, and either a carbon atom, R^1 , R^2 and R^3 have combined the remaining P.]

[0023] A vinyl system polymer which has a functional group at the end of the invention according to claim 4. In a vinyl system polymer which has a functional group at the end expressed with the general formula (1) according to claim 1, (C, R^1, R^2, R^3) are $CHR^{10} - Ar - CHR^{11} - (Ar - R) - CHR^{11}$ or $CHR^{10} - (R - Ar - R) - CHR^{11}$ (among a formula). An aromatic ring in which Ar has an aromatic ring or one or more substituents, and R express an aliphatic group, and R^{10} and R^{11} express an alkyl group or an aryl group of straight chain shape of the carbon numbers 1-20, or branching respectively. It is expressed.

[0024] A vinyl system polymer which has a functional group at the end of the invention according to claim 5. In a vinyl system polymer which has a functional group at the end expressed with the general formula (2) according to claim 2, $(C, R^1, R^2, R^3) - Ar - CHR^{10} - (Ar - R) - CHR^{10}$, or $(R - Ar - R) - CHR^{10}$ (Ar among a formula). An aromatic ring and R^{10} which have an aromatic ring or one or more substituents express an alkyl group or an aryl group of straight chain shape of the carbon numbers 1-20, or

branching. It is expressed.

[0025] A vinyl system polymer which has a functional group at the end of the invention according to claim 6. In a vinyl system polymer which has a functional group at the end expressed with the general formula (3) according to claim 3, $(C, R^1, R^2, R^3) - Ar - (CHR^{10}) - (CHR^{11}) \dots - (CHR^{10z-2}) - (CHR^{10z-1}) \dots - (Ar - R) - (CHR^{10}) - (CHR^{11}) \dots - (CHR^{10z-2}) - (CHR^{10z-1}) \dots - (CHR^{10z-2}) - (CHR^{10z-1})$ [As for an aromatic ring in which Ar has an aromatic ring or one or more substituents, and Z, an integer of 3-6, R^{10} , R^{11} , R^{10z-2} , and R^{10z-1} express an alkyl group or an aryl group of straight chain shape of the carbon numbers 1-20, or branching respectively among a formula. It is expressed with].

[0026] A vinyl system polymer which has a functional group at the end of the invention according to claim 7. In a general formula which expresses with claims 1-5 or an end given in 6 a vinyl system polymer which has a functional group, it is that acrylic ester (meta) of a copolymer is independent or what of a vinyl system monomer which is shown by P and in which a radical polymerization is possible is independent or that is a copolymer.

[0027] A vinyl system polymer which has a functional group at the end of the invention according to claim 8. In a general formula which expresses with claims 1-5 or an end given in 6 a vinyl system polymer which has a functional group, it is that acrylonitrile (meta) of a copolymer is independent or what of a vinyl system monomer which is shown by P and in which a radical polymerization is possible is independent or that is a copolymer.

[0028] In a vinyl system polymer in which a vinyl system polymer which has a functional group at the end of the invention according to claim 9 has a functional group at claims 1-7 or the end of an invention given in 8, number average molecular weights are 500-50000, and an end functional group introduction rate is not less than 90%.

[0029] A manufacturing method of a vinyl system polymer which has a functional group at the end of the invention according to claim 10. It is a manufacturing method of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9. It is general formula $NH(R^4) - R^5 - X$ to a polymer which polymerized and was produced by ranking second in a vinyl system monomer, using an iodine content compound which contains in intramolecular at least one iodine atoms combined with a carbon atom of a side chain of an aromatic ring as a chain transfer agent. [Each of X, R^4 , and R^5 is the same as that of the contents of the agreement in a general formula (1) among a formula. An amine compound expressed with] is made to react, and a functional group is introduced into a molecular terminal.

[0030] A hardenability constituent of the invention according to claim 11 becomes considering a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 as the main ingredients.

[0031] A hardenability constituent of the invention according to claim 12 contains a compound which contains a functional group of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9, and the above-mentioned end, and a functional group in which a reaction is possible in [two or more] a molecule.

[0032] A functional group of an end of a vinyl system polymer in which a hardenability constituent of the invention according to claim 13 has a functional group at claims 1-8 or the end given in 9 is a hydroxyl group. A compound which contains a functional group in which this and a reaction are possible in [two or more] a molecule contains at least one sort of compounds chosen from a group of a polyfunctional isocyanate compound, melamine resin, and urea resin.

[0033] A functional group of an end of a vinyl system polymer in which a hardenability constituent of the invention according to claim 14 has a functional group at claims 1-8 or the end given in 9 is a carboxyl group. A compound which contains a functional group in which this and a reaction are possible in [two or more] a molecule contains at least one sort of compounds chosen from a group of a polyfunctional isocyanate compound, a polyfunctional epoxy compound, and a polyfunctional aziridine compound.

[0034] A functional group of an end of a vinyl system polymer in which a hardenability constituent of the invention according to claim 15 has a functional group at claims 1-8 or the end given in 9 is a silyl group. A compound which contains a functional group in which this and a reaction are possible in [two or more] a molecule contains at least one sort of compounds chosen from a group of a

multivalent hydrosilyl compound, a multivalent hydrogen silicone compound, a multivalent alkoxy silyl compound, and silica.

[0035] A functional group of an end of a vinyl system polymer which has a functional group at claims 1-8 or the end given in 9 is a vinyl group, and a hardenability constituent of the invention according to claim 16 contains this and a vinyl system monomer which contains at least one polymerization nature unsaturation group in intramolecular.

[0036] An end functional group of a vinyl system polymer which has a functional group at the end of this invention, Especially if it does not separate temporally, it is not limited, but a hydroxyl group, a carboxyl group, a silyl group, an alkenyl group, a halogen group, an amino group, a thionyl group, an epoxy group, an ethynyl group, a sulfinyl group, an oxazoline group, a malonimide group, an azlactone group, etc. are mentioned, for example. Especially, a hydroxyl group, a carboxyl group, a silyl group, and an alkenyl group are used suitably.

[0037] Especially as the above-mentioned silyl group, although not limited, for example A trihydro silyl group, A methyl dihydrosilyl group, a dimethyl hydrosilyl group, an ethyl dihydrosilyl group, A diethyl hydrosilyl group, a trimethoxysilyl group, a methyl dimethoxy silyl group, A dimethyl methoxy silyl group, an ethyl dimethoxy silyl group, a diethyl methoxy silyl group, A triethoxy silyl group, a methyl diethoxy silyl group, a dimethylethoxy silyl group, an ethyldiethoxy silyl group, a diethylethoxy silyl group, the Tori (isopropoxy) silyl group, the Tori (n-butoxy) silyl group, etc. are mentioned.

[0038] A vinyl system polymer which has a functional group at the end of this invention is characterized by having an amide group near the end of a molecule. For this reason, depending on a kind of end functional group, the reactivity of end functional groups, and an end functional group and a compound in which a reaction is possible is improved. For example, an end functional group of a vinyl system polymer which has a functional group at the end of this invention is a hydroxyl group, and it acts as a catalyst because an amide group is near a hydroxyl group in making this and an isocyanate compound react, and the reactivity becomes high as compared with a case where there is no amide group. When an end functional group of a vinyl system polymer which has a functional group at the end of this invention is alkoxy silyl groups, the reactivity of alkoxy silyl groups is improved because an amide group is near alkoxy silyl groups. Since time which hardening takes is shortened, intensity of a hardened material is revealed at an early stage, and a hardenability constituent containing a vinyl system polymer which has alkoxy silyl groups in this end is excellent in workability.

Especially when R⁴ is a hydrogen atom, a vinyl system polymer obtained serves as structure with secondary amine near an end, and a hardening reaction becomes easy to be promoted.

[0039] Although a vinyl system monomer in particular used by this invention is not limited, For example, when using acrylic ester (meta) as the main ingredients, chain extension or a hardened material made reticulated of a vinyl system polymer which has a functional group at the end obtained is excellent in transparency, and excellent in weatherability, heat resistance, and a water resisting property, and excellent in an adhesive property. The above-mentioned performance occurs, when used combining other vinyl system monomers, if a rate of acrylic ester (meta) is 50 % of the weight or more, an improvement effect of each above-mentioned performance will be accepted, and if it is considered as 100% of acrylic ester (meta), each above-mentioned performance will improve notably.

[0040] Especially as the above-mentioned (meta) acrylic ester, although not limited, For example, methyl acrylate (meta), ethyl acrylate (meta), acrylic acid (meta) n-propyl, (Meta) Acrylic acid isopropyl, acrylic acid (meta) n-butyl, (Meta) Isobutyl acrylate, acrylic acid (meta) tert-butyl, (Meta) Acrylic acid pentyl, acrylic acid (meta) n-hexyl, acrylic acid (meta) isohexyl, (Meta) Acrylic acid n-octyl, acrylic acid (meta) isooctyl, (Meta) 2-ethylhexyl acrylate, acrylic acid (meta) nonyl, (Meta) Decyl acrylate, acrylic acid (meta) dodecyl, acrylic acid (meta) phenyl, (Meta) Acrylic acid toluyl, acrylic acid (meta) benzyl, acrylic acid (meta) stearyl, (Meta) Acrylic acid 2-hydroxyethyl, KISHIRU, acrylic acid (meta) 3-methoxy propyl, Acrylic acid (meta) fluoro alkyl ester, acrylamide (meta), acrylic acid (meta), etc. by which some or all of an alkyl group of a hydrogen atom was replaced with a fluorine atom are mentioned. [of the carbon numbers 1-20] Two or more sorts may be put together and these (meta) acrylic ester may be used together, although it may be used independently.

[0041] When changing to the above-mentioned (meta) acrylic ester and using acrylonitrile (meta) as the main ingredients, chain extension or a hardened material made reticulated of a vinyl system polymer which has a functional group at the end obtained becomes the thing excellent in oil resistance and gas barrier property. The above-mentioned performance occurs, when used combining

other vinyl system monomers, if a rate of acrylonitrile (meta) is 50 % of the weight or more, an improvement effect of each above-mentioned performance will be accepted, and if it is considered as acrylonitrile (meta) 100%, each above-mentioned performance will improve notably.

[0042] In general formula (1) - (3) which expresses with an end of the invention according to claim 1 to 3 a vinyl system polymer which has a functional group, (C, R¹, R², R³) Among an ingredient and among R¹, R², and R³, although either can take a -Ar-mold, a -Ar-R-mold, or a -R-Ar-R-mold aromatic ring (however, Ar expresses an aromatic group and R expresses an aliphatic group), Ar is an aromatic ring which has aromatic rings, such as the benzene ring, a naphthalene ring, an anthracene ring, and a biphenyl ring, or one or more substituents, and R means a -Ar-R-mold or a -R-Ar-R-mold aromatic ring equivalent to an alkyl group.

[0043] They are [in / in a general formula which expresses with an end of the invention according to claim 4 to 6 a vinyl system polymer which has a functional group / a -Ar-mold, a -Ar-R-mold, or a -R-Ar-R-mold aromatic ring / general formula (1) - (3)] the same contents.

[0044] In general formula (1) - (3) which expresses with an end of the invention according to claim 1 to 6 a vinyl system polymer which has a functional group, (C, R¹, R², R³) As R¹, R², and R³, among an ingredient, hydrogen, halogen, and an alkyl group of the carbon numbers 1-20 — desirable — 1-10 — more — desirable — an alkyl group of 1-6. A cycloalkyl group of the carbon numbers 3-8, C(=Y) NR⁶R⁷, C(=Y) R⁸, a carboxylic acid chloride group, a hydroxyl group, a cyano radical, an alkenyl group of the carbon numbers 2-20, and an alkenyl group of the carbon numbers 2-20 — desirable — an alkenyl group of 2-6, or an alkenyl group. More preferably A vinyl group, a oxilanyl group, a glycidyl group, an allyl group, An aryl group, a -Ar-mold, -(Ar-R)-mold aromatic ring, or -(R-Ar-R)-mold aromatic ring, however, an aromatic ring in which Ar has an aromatic ring or one or more substituents. A heterocyclyl group with which R expresses an aliphatic group, an aralkyl group, an ARARUKENIRU group, an alkyl group of the carbon numbers 1-6 which until all replaced by a halogen atom from one of a hydrogen atom and an alkoxy group of the carbon numbers 1-4, an aryl group, a heterocyclyl group, C(=Y) NR⁶R⁷. Although an alkyl group, an OKIRANIRU group, or a glycidyl group of the carbon numbers 1-6 replaced by 1 to three bases chosen from a group of C(=Y) R⁸ is mentioned, it is two or less pieces that both R¹, R², and R³ can take hydrogen. R⁴ expresses hydrogen, an alkyl group of the carbon numbers 1-6, an alkenyl group of the carbon numbers 1-6, an aryl group, a phenyl group, or benzyl — R⁵. In an alkyl group (preferably 1-10, more preferably alkyl group of 1-6) of the carbon numbers 1-20, its main chain, or a side chain, an ester group. Either of the alkyl groups (preferably 1-10, more preferably alkyl group of 1-6) of the carbon numbers 1-20 containing one or more polar groups or aromatic rings which were chosen from a group which consists of an amide group, an amino group, a urethane group, a sulfinyl group, a vinyl group, and the benzene ring is expressed. Y is NR⁹ or an oxygen atom, and NR⁶R⁷. An alkyl group of the carbon numbers 1-5 or a cycloalkyl group of the carbon numbers 1-5 which both R⁶ and R⁷ combined with a nitrogen atom, Or R⁶ and R⁷ join together, and an alkylene group of the carbon numbers 2-5 is formed. A thing in which an annular group of 3 which forms a nitrogen atom and an annular group of 3 - 6 member, or has a side chain - 6 members was formed is expressed, R⁸ is an alkyl group of the carbon numbers 1-20, an alkoxy group of the carbon numbers 1-20, an aryloxy group, or a heterocyclyl oxy group, and R⁹ expresses an alkyl group or an aryl group of hydrogen, a straight chain, or the carbon numbers 1-20 of branching.

[0045] As the above-mentioned aryl group, phenyl, naphthyl, phenan tolyl, phenalenyl, Anthracenyl, TORIFENIRU, fluoran thenyl, prenyl, Penta SENIRU, KURISENIRU, NAFTA SENIRU, hexaphenyl, PISENIRU, Say pilus RENIRU (suitably phenyl and naphthyl), and here each hydrogen atom And alkyl of the carbon numbers 1-20 (more suitably methyl [Suitably the carbon numbers 1-6]), Alkyl of the carbon numbers 1-20 by which each of a hydrogen atom was independently replaced with a halogenide (suitably fluoride or a chloride) (more suitably methyl [Suitably the carbon numbers 1-6]), Alkenyl of the carbon numbers 1-20, alkynyl of the carbon numbers 1-20, alkoxy [of the carbon numbers 1-6] **, Alkylthio of the carbon numbers 1-6, cycloalkyl of the carbon numbers 3-8, phenyl, It may be replaced by phenyl replaced by an alkyl group of halogen, NH₂, alkylamino of the carbon numbers 1-6, dialkylamino of the carbon numbers 1-6 and 1-5 halogen atoms, and/or the carbon

numbers 1-4, (A definition of "aryl" is defined also as an aryl group in "aryloxy" and an "aryalkyl") So, 1-5 phenyl may be replaced by one of the above-mentioned substituents, and 1-7 naphthyls are replaced --- **** (when an aryl group is replaced suitably, 1-3 pieces are replaced.) --- suitable --- "aryl" --- phenyl. Phenyl replaced by phenyl replaced with naphthyl, fluoride, or 1-5 chlorine and alkyl of the carbon numbers 1-6, and 1-3 substituents chosen from a group which consists of alkoxy **** phenyl of the carbon numbers 1-4 is said. "Aryl" says phenyl, tolyl, and methoxyphenyl most suitably. [0046]As Ar in the above-mentioned --Ar--mold, --(Ar-R)--mold aromatic ring, or --(R-Ar-R)--mold aromatic ring, it is an aromatic ring which has aromatic rings, such as the benzene ring, a naphthalene ring, an anthracene ring, and a biphenyl ring, or one or more substituents, and a --Ar-R--mold or a --R-Ar-R--mold aromatic ring equivalent to an aralkyl group is meant as R.

[0047]As the above-mentioned heterocyclyl group, pyridyl, a furil, pyrrolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl one, pyrimidinyl, pyridazinyl, Pyranyl, indolyl, isindolyl, indazolyl, a benzo furil, An isobenzofuril, benzo thienyl, isobenzothienyl, clo MENIRU, KISAN thienyl, Puri Nils, PUTERJINIRU, quinolyl, isokinolyl, Phthalazinyl, chinae-cortex ZORINIRU, kino SARINIRU, naphthyridinyl, FENOKISACHI inyl, Carbazoyl, SHINORINIRU, phenanthridinyl, acridinyl, 1, 10-phenan trolley nil. Those known hydrogenation gestalten are said to FENA-JINIRU, phenoxazinyl, phenothiazinyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, and a specialist in the art concerned. Pyridyl, a furil, prolyl, thienyl, imidazolyl, pyrazolyl, pyrazinyl one, pyrimidinyl, pyridazinyl, pyranyl, and indolyl are included by suitable heterocyclyl group, and the most suitable heterocyclyl group is pyridyl.

[0048]Expressing an alkenyl group by which aryl group substitution was carried out as the above-mentioned ARARUKENIRU group, an aryl group is as having mentioned above here, and an alkenyl group expresses a vinyl group which may be replaced with an alkyl group and/or a halogen atom of the carbon numbers 1-6 of one piece or two pieces.

[0049]When a carbon number of an alkyl group of the above-mentioned carbon numbers 1-20, an alkenyl group of the carbon numbers 2-20, an alkenyl group of the carbon numbers 2-20, and an alkoxy group of the carbon numbers 1-20 becomes larger than 20, an end of this invention has a possibility that the adhesive property of a hardenability constituent containing a vinyl system polymer which has a functional group may worsen.

[0050]A molecular weight of a vinyl system polymer which has a functional group at the end of this invention, A lot of [although not limited in particular / if not much small, in order to stiffen a hardenability constituent containing the above-mentioned polymer] hardening agents are needed, Since the productivity of a hardened material and deterioration of quality, such as hardenability falling, cure time becoming long, or reducing hardened material physical properties since hardening is not fully performed, will be caused if it is not practical and is not much large, a number average molecular weight --- desirable --- 500-100,000 --- it is 500-50,000 still more preferably.

[0051]Although not limited, since hardening is not fully performed and especially an end functional group introduction rate of a vinyl system polymer which has a functional group at the end of this invention has a possibility of reducing hardened material physical properties when it is not much low, it is not less than 90% preferably.

[0052]A manufacturing method of a vinyl system polymer which has a functional group at the end of this invention, Although not limited in particular, preferably, A vinyl system monomer is polymerized and ranked second, using an iodine content compound which contains in intramolecular at least one iodine atoms combined with a carbon atom of a side chain of an aromatic ring as a chain transfer agent, It is general formula $\text{NH}(\text{R}^4)-\text{R}^5-\text{X}$ (X, R^4 , and R^5 among a formula) to an obtained polymer. All are the same as that of the contents of the agreement in a general formula (1). An amine compound expressed is made to react and a manufacturing method of a vinyl system polymer which has a functional group is mentioned to an end which introduces a functional group into a molecular terminal.

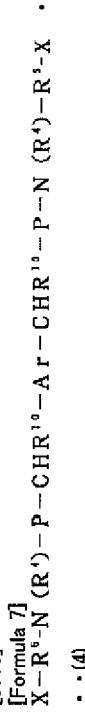
[0053]An aromatic ring which constitutes the above-mentioned iodine content compound, Although not limited in particular, aromatic rings, such as the benzene ring, a naphthalene ring, and an anthracene ring, were mentioned, it had one or more substituents combined with an aromatic ring with a carbon atom in these aromatic rings, and at least one or more iodine atoms are combined with them via a carbon atom of this substituent, for example. In the above-mentioned aromatic ring, as long as it does not check a radical polymerization reaction, it may have substituents other than the above. Although an alkyl group, an alkoxy group, an amino group, a hydroxyl group, a halogen group, a

carbonyl group, a carboxyl group, a thionyl group, etc. are mentioned and these may exist by a single species as these substituents, for example, two or more sorts may exist.

[0054]It is made easy for binding energy of a carbon-halogen bond to fall and to happen in radical dissociation of a carbon-halogen bond, since an electron donative group which becomes the carbon atom which iodine atoms combined from an aromatic ring etc. has combined an iodine content compound which iodine atoms combined with the above-mentioned structure. Since an electron donative group consists of aromatic rings etc. as mentioned above, the chain transfer nature of a carbon radical which a radical stabilization effect by a pi electron of an aromatic ring showed up notably, and generated becomes high, and it becomes easy to control it of a request polymerization reaction.

[0055]As a chain transfer agent of the above-mentioned structure, it is general formula $\text{I}(\text{CHR}^{10}-\text{Ar}-\text{CHR}^{10})_n$ [Ar and R^{10} express a basis of said general formula (1) and the contents. When using], a vinyl system polymer which has a functional group at the end obtained serves as structure expressed with a said general formula (1) type following general formula (4).

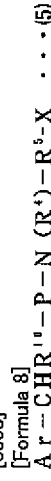
[0056]



[Formula 7]

[0057]As a chain transfer agent, it is general formula $\text{Ar}-\text{CHR}^{10}$, [Ar and R^{10} express the basis of said general formula (1) and the contents. When using], the vinyl system polymer which has a functional group at the end obtained serves as structure expressed with a said general formula (2) type following general formula (5).

[0058]

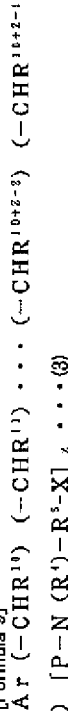


[Formula 8]

[0059]It is the general formula $\text{Ar}(-\text{CHR}^{10})_n(-\text{CHR}^{11})_m$ as a chain transfer agent... $(-\text{CHR}^{10}-\text{Z}-\text{Z}^2)$ $(-\text{CHR}^{10}-\text{Z}-\text{Z}^2)_n$ [Ar, R^{10} , and Z express the basis of said general formula (1) - (3) and the contents.

When using], the vinyl system polymer which has a functional group at the end obtained serves as structure expressed with a said general formula (3) type following general formula (6).

[0060]



[Formula 9]

[0061]The iodine content compound used as a chain transfer agent, Especially if it is aromatic compounds which have combined at least one or more iodine atoms via the carbon atom of the substituent described above, are not limited, but. For example, 1,3-bis(iodomethyl)benzene, 1,4-bis(iodomethyl)benzene, 1,3,5-tris(iodomethyl)benzene, diphenyl diiodomethane, 4,4'-bis(iodomethyl)biphenyl, a screw (4-iodo methyl)phenyl, 2,6-bis(iodomethyl)naphthalene, 2,4,6,8-tetrakis(iodomethyl)naphthalene, 2,6-bis(iodomethyl)anthracene, 9,10-bis(iodomethyl)anthracene, 2,4,5,8-tetrakis(iodomethyl)anthracene, etc. are mentioned, and the compound which contains two iodine atoms in a molecule especially is used suitably.

[0062]It may have substituents other than the above if needed in a carbon atom of a substituent which combined with the above-mentioned aromatic ring and has combined iodine atoms. Although an alkyl group, an alkoxy group, an amino group, a hydroxyl group, a halogen group, a carbonyl group, a carboxyl group, a thionyl group, etc. are mentioned and these may exist by one sort as these substituents, for example, two sorts may exist.

[0063]In an aromatic ring of these iodine content compounds, as long as it does not check a radical polymerization reaction, it may have a substituent which has not combined the above-mentioned iodine atoms if needed. Although an alkyl group, an alkoxy group, an amino group, a hydroxyl group, a halogen group, a carbonyl group, a carboxyl group, a thionyl group, etc. are mentioned and these may exist by a single species as these substituents, for example, two or more sorts may exist.

[0071] This can be used for a vinyl system polymer which has a functional group at the end obtained by invention given in claims 1-8 or 9 as a hardenability constituent which becomes as a subject. Although the above-mentioned hardenability constituent can also be constituted from an above-mentioned polymer independent as a hardenability ingredient according to a kind of functional group which the above-mentioned polymer has, it can also have composition which contains a compound which contains a functional group of an end which the above-mentioned polymer and the above-mentioned polymer have, and a functional group in which a reaction is possible in [two or more] a molecule as a hardenability ingredient.

[0079] Although a compound in particular that has two or more amino groups in the above-mentioned

intramolecular is not limited, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, hexamethylenediamine, etc. are mentioned, for example.

[0080]In a hardenability constituent of the invention according to claim 15 whose functional group (X) of the above-mentioned polymer is a silyl group. The above-mentioned multivalent hydrosilyl compound or a multivalent hydrogen silicone compound among compounds which contain a functional group in which functional group (X) of an end of the above-mentioned polymer and a reaction are possible in [two or more] a molecule. Although not limited in particular, either a publicly known multivalent hydrosilyl compound or a multivalent hydrogen silicone compound can be used, for example. Although it is not the above-mentioned multivalent alkoxyisilyl compound, especially a thing limited, all of a publicly known multivalent alkoxyisilyl compound can be used, for example.

[0081]As a silyl group in the above-mentioned multivalent hydrosilyl compound and a multivalent alkoxyisilyl compound. For example, a trihydro silyl group, a methylidi hydrosilyl group, an ethyl dihydrosilyl group, a trimethoxyisilyl group, a methyl dimethoxy silyl group, an ethyl dimethoxy silyl group, an ethyldiethoxy silyl group, the Tori (isopropoxy) silyl group, the Tori (n-propoxy) silyl group, the Tori (n-butoxy) silyl group, etc. are mentioned.

[0082]In a hardenability constituent of the invention according to claim 16 whose functional group (X) of the above-mentioned polymer is a vinyl group, A vinyl system monomer which has at least one polymerization nature unsaturation group in the above-mentioned intramolecular of a compound which contains a functional group in which functional group (X) of an end of the above-mentioned polymer and a reaction are possible in [two or more] a molecule. Although not limited in particular, for example in a general formula (1) described above, a vinyl system monomer etc. which can polymerize by a polymerization method of the same vinyl system monomer as a vinyl system monomer which constitutes a polymer or a copolymer expressed with P, and in which a radical polymerization is possible, etc. and others are mentioned.

[0083]A various application of an adhesive, a sealing agent, elastic adhesives, a paint, foam, a film, thermoplastic elastomer, a sound deadener, various molding materials, a resin modifier, a gel coat agent, artificial marble, etc. is presented with claims 11-15 or a hardenability constituent of an invention given in 16.

[0084]

[Embodiment of the Invention]Although the example of this invention is given to below and explained to it in more detail, this invention is not limited only to these examples.

[0085](Example 1) 100 g of butyl acrylate, the 1,4-bis(iodomethyl)benzene 4.0g. After scaling 0.8g of 2,2'-azobisisobutyronitrile, and 100 g of toluene to the 1 liter-capacity 4 Thu mouth separable flask and attaching separable covering, stirring wings, a three-way cock, a condenser tube, and a temperature probe, the nitrogen purge of the inside of a polymerization vessel was carried out in bubbling. Passing nitrogen gas, it stirred at 100 rpm, the inside of a polymerization vessel was maintained at 60 **, and the polymerization reaction was continued for 5 hours. The conversion of 5 hours after was 96%.

[0086]In order to change the end group of the obtained polymer after the end of a polymerization, 3.0 g of 2-aminoethanol is added, After making it react at 100 ** for 20 hours, the vinyl system polymer which carries out distillation under reduced pressure of said unreacted monomer, the above-mentioned end group displacing agent, and the solvent, removes them at 150 **, washes a polymer with methanol, carries out reduced pressure drying at 100 ** further for 5 hours, and has a functional group at the end was produced.

[0087](Examples 2-13) The vinyl system polymer which has a functional group at the end like Example 1 on the polymerization conditions, end group displacing agent, and substitution conditions which are indicated to the table was produced using the vinyl system monomer, the iodine content compound, the polymerization initiator, catalyst, and solvent which are respectively indicated to Table 1.

[0088]

[Table 1]

2AB: 2-アミノエタノール
APMDS: 3-アミノプロピルジメチルシラン
PMS: 2-アミノエタノール

BMBS: 1,4-ビス(3-メチルブチル)ベンゼン
TMB: 1,3,5-トリメチルベンゼン
BMS: 4-メチルベンゼン
SMB: 2-メチルブチルベンゼン
AIBN: 2-アゾビスイソブチロニトリル

EMA: 7-リノール酸 2-エチルヘキシル
MMA: 4-オクチル酸
BA: 7-リノール酸
SMA: 7-リノール酸
AN: 7-リノール酸

実施例	1	2	3	4	5	6	7	8	9	10	11	12	13
モノマー	EMA	BA	BA	EMA	BA	EMA	BA	EMA	BA	EMA	BA	EMA	BA
重合剤	100	100	100	100	100	100	100	100	100	100	100	100	100
重合温度	100℃	100℃	100℃	100℃	100℃	100℃	100℃	100℃	100℃	100℃	100℃	100℃	100℃
重合時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間	20時間
重合率	96	90	90	92	90	94	90	95	90	95	90	91	90
重合条件	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間	100℃×20時間

[0089]The functional group number of the number average molecular weight of the vinyl system polymer which has a functional group at the end obtained in above-mentioned Examples 1-13, weight average molecular weight, molecular weight distribution (ratio of weight average molecular weight to a number average molecular weight), and an end was measured by the method shown below. A measurement result is shown in Table 2.

[0090]1. A number average molecular weight, weight average molecular weight, and molecular weight distribution : gel PAMIESHON column chromatograph which used tetrahydrofuran for eluent it measured using [GPC (column: the Showa Denko K.K. make, "KF-80M" 42 **)], and computed by polystyrene reference standard conversion. Only about the vinyl system polymer which has a functional group at the end obtained in Example 8, 5mM lithium bromide / dimethylformamide solution was used for the eluent, and the column was changed into the Showa Denko K.K. make, "KD-805",

the above-mentioned adhesives are applied so that the thickness after desiccation may be set to 10 micrometers. The 50-micrometer-thick OPP film was laminated on it, it was neglected for seven days at 40 °* by this state, the sample was created, and T type friction test was done by a part for speed-of-testing/of 300 mm using Instron. A test result is shown in Table 3.

[0106][Comparative example 3] The adipic acid 57g, 7 g of 1,4-butanediol, 36g of 1,6-hexanediol, and 0.5 g of titanium tetra isopropoxy sides. After scaling to four 1 liter-capacity mouth separable flask and attaching separable covering, stirring wings, a three-way cock, and a temperature probe, the inside of the above-mentioned polymerization vessel was stirred at 200 °* for 1 hour. Subsequently, decompressing the system of reaction to 50orr, heating stirring was performed at 270 °* for 3 hours, the polycondensation was advanced, the polyester system polymer was obtained, it dissolved in the solvent, and adhesives were produced. Two 50-micrometer-thick OPP films were pasted up for the obtained adhesives like Example 16, the sample was created, and T type friction test was done by a part for speed-of-testing/of 300 mm using Instron. A test result is shown in Table 3.

[0107]Adhesive strength (T type friction test) was remarkable to the conventional polyester system adhesives with which the adhesives using the hardenability constituent of this invention of the above-mentioned Example 16 were shown in the comparative example 3, and it was high.

[0108][Example 17] The vinyl system polymer 50g which has a functional group at the end obtained in Example 2, The vinyl system polymer 20g which has a functional group at the end obtained in Example 3, the vinyl system polymer 30g which has a functional group at the end obtained in Example 8, and "coronate L" 4.5g were dissolved in the partially aromatic solvent of 100 g of 200g of toluene / dimethylformamide, and adhesives were produced

[0109]On a 50-micrometer-thick PET film, the obtained adhesives are applied so that the thickness after desiccation may be set to 10 micrometers. It dried for 10 minutes at 120 °*, and the 50-micrometer-thick PET film was laminated on it, it was neglected for seven days at 40 °* by this state, the sample was created, and T type friction test was done by a part for speed-of-testing/of 300 mm using Instron. T type friction test was similarly done as an oil resistance test about what immersed the above-mentioned sample in 80 °* JIS No. 3 oil (rubber processing oil) for 72 hours. A test result is shown in Table 3.

[0110][Comparative example 4] Two 50-micrometer-thick PET films were pasted up for the adhesives obtained by the comparative example 3 like Example 17, the sample was created, and T type friction test was done by a part for speed-of-testing/of 300 mm using Instron. A test result is shown in Table 3.

[0111]It turns out that the adhesives using the hardenability constituent of this invention of the above-mentioned Example 17 have the oil resistance outstanding to the conventional polyester system adhesives shown in the comparative example 3.

[0112][Example 18] 90 g of hydroxypropyl methacrylate, 0.2 g of acid phosphoric acid triethyl ester, 5 g of t-butyl peroxide, 0.1 g of p-benzoquinone, the hydroxyacetone 1.5g, and ABS plastics (made in **** Naugatuck.) "Kula Russ Chick 2540A" To 30 g, the vinyl system polymer 10g which has a functional group was added to the end obtained in Example 13, stirring mixing was carried out, adhesives were produced, and it applied to the general structural-steel board by brush coating.

[0113]Change to the hydroxyacetone 1.5g of the above-mentioned adhesives, and adhesives are produced using 1.5 g of vanadium acetylacetonato. It applied to the general structural-steel board different from this by brush coating, it pasted together so that an adhesive application side might paste up the steel plate of two sheets, and it was recuperated for one day at 23 °*, the sample was created, and T type friction test was done by a part for speed-of-testing/of 300 mm using Instron. A test result is shown in Table 3.

[0114][Comparative example 5] It changes to the vinyl system polymer 10g which has a functional group at the end obtained in Example 13, Except having used 10 g of dimethacrylate of the ethyleneoxide addition of bisphenol A, two kinds of adhesives were produced like Example 18, the steel plate of two sheets was pasted together similarly, the sample was created, and T type friction test was done by a part for speed-of-testing/of 300 mm using Instron. A test result is shown in Table 3.

[0115]It turns out that the adhesives using the hardenability constituent of this invention of the above-mentioned Example 18 have the adhesive strength outstanding to the conventional 2 liquid acrylic adhesives shown in the comparative example 5.

[0116][Example 19] acrylic polyol (the Dainippon Ink chemicals company make and "AKURIDIKKU DL-1573") 55% of solid content [150 g of], the titanium dioxide 100g, 8.0 g of diphenylmethane diisocyanate, In 0.5g of dibutyltin dilaurate, and 300 g of toluene, the vinyl system polymer 50g which has a functional group was added to the end obtained in Example 6, stirring mixing was carried out, and the hardenability constituent (acrylic urethane paint) was produced.

[0117]On the OPP film with a thickness of 75 micrometers which carried out corona discharge treatment of the above-mentioned hardenability constituent, it applied so that the thickness after desiccation might be set to 25 micrometers, and it dried for 20 minutes in 150 °* oven, and the coat was formed. In order to evaluate the performance of the above-mentioned hardenability constituent, the break with a size of 10 mm x 10 mm in a grid pattern was put in all directions [of the coat]. 100 masses were made, the cross out adhesion test which sticks and tears off a cellophane tape on this mass was done, and the number of masses of the coat which separated was measured. After folding up the OPP film painted [above-mentioned] at the angle of 180 degrees, the bending test which develops this in the original state was done, and it examined visually whether the white bluish mark and the crack occurred on the fold of the coat, and evaluated in two steps, thing:O to which neither a white bluish mark nor a crack is accepted, and thing:x** which the white bluish mark and the crack generated. The result was shown in Table 4.

[0118][Example 20] The inside of the hardenability constituent (acrylic urethane paint) of Example 19, Decrease the quantity of the loadings of acrylic polyol from 150g to 100 g, and it changes to the vinyl system polymer 50g which has a functional group at the end obtained in Example 6, Except having used the vinyl system polymer 100g which has a functional group for the end obtained in Example 7, the hardenability constituent (acrylic urethane paint) was produced like Example 19, and the performance was evaluated similarly. The result was shown in Table 4.

[0119][Comparative example 6] The inside of the hardenability constituent (acrylic urethane paint) of Example 19, The quantity of the loadings of acrylic polyol was increased from 150g to 200 g, and except not having blended the vinyl system polymer which has a functional group at the end of this invention, the hardenability constituent (urethane paint) was produced like Example 19, and the performance was evaluated similarly. The result was shown in Table 4.

[0120]

[Table 4]

用 途	実 施 例		比 較 例	実 施 例		比 較 例	実 施 例		比 較 例
	19	20		21	22		7	8	
ねじり試験 (100mm間隔)	0	0	3 5	-	-	-	-	-	-
曲げ試験	○	○	×	-	-	-	-	-	-
破断強度 (kg/cm ²)	-	-	-	2 5 0	2 3 0	2 2 0	1 1 0	2. 1	1. 5
破断伸び (%)	-	-	-	6 3 0	5 7 0	5 9 0	7 5 0	5 5 0	5 3 0
耐熱性試験 (熱変形率 %)	-	-	-	9 4	8 6	8 1	3 0	9 5	8 0

[0121]It turns out that the acrylic urethane paint using the hardenability constituent of this invention of Example 19 and Example 20 has the performance which was extremely excellent in both the adhesive property of a coat, and bendability-proof as compared with the conventional acrylic urethane paint of the comparative example 6 which did not use this so that more clearly than Table 4.

[0122][Example 21] To the vinyl system polymer 25g which has a functional group at the end obtained in the vinyl system polymer 75g and Example 5 which have a functional group at the end obtained in Example 3, 2.5g of isophorone diisocyanate and 0.5 g of dibutyltin dilaurate were added, by Plast Mill, kneading mixing was carried out for 20 minutes, and 200 °* of thermoplastic poly block copolymers were produced.

[0123]The 1-mm-thick sheet was produced using the pressing machine, and a physical-properties

examination (at the time of a fracture tensile strength, elongation) and weathering test (strength retention) of a normal state were presented with the above-mentioned thermoplastic poly block copolymer. The above-mentioned physical-properties examination was done based on JIS K 8301, using the sunshine weatherometer, under the environment of 50 °C and 65%RH, UV irradiation of the weathering test was carried out, and it was done. The test result was shown in Table 4.

[0124](Example 22) The vinyl system polymer 50g which has a functional group at the end obtained in Example 8, The vinyl system polymer 100g and 0.5 g of dibutyltin dilaurate which have a functional group at the end obtained in Example 9, Decompressing the inside of the above-mentioned polymerization vessel to 5torr, after sealing to four 1 liter-capacity mouth separable flask and attaching separable covering, stirring wings, a three-way cock, and a temperature probe, heating stirring was performed at 200 °C for 3 hours, the polycondensation was advanced, and the thermoplastic poly block copolymer was produced. About the obtained thermoplastic poly block copolymer, a physical-properties examination and weathering test of a normal state were done like Example 21. The test result was shown in Table 4.

[0125](Comparative example 7) 50 g of naphthalene-dicarboxylic-acid dimethyl, the adipic acid 30g, After sealing 50g of ethylene glycol, and 0.5 g of titanium tetra isopropanol POKSAIDO to four 1 liter-capacity mouth separable flask and attaching separable covering, stirring wings, a three-way cock, and a temperature probe, the inside of the above-mentioned polymerization vessel was stirred at 200 °C for 1 hour. Subsequently, decompressing to 5torr, heating stirring was performed at 270 °C for 3 hours, the polycondensation was advanced, and the thermoplastic poly block copolymer was produced. About the obtained thermoplastic poly block copolymer, a physical-properties examination and weathering test of a normal state were done like Example 21. The test result was shown in Table 4.

[0126](Comparative example 8) About the thermoplastic elastomer which consists of styrene butadiene styrene block copolymer (SBS, 35 % of the weight of styrene content), a physical-properties examination and weathering test of a normal state were done like Example 21. The test result was shown in Table 4.

[0127]The acrylic thermoplastic elastomer using the hardenability constituent of this invention of Example 21 and Example 22 so that more clearly than Table 4, It turns out that it has the outstanding physical properties and especially outstanding weatherproof performance of a normal state as compared with the conventional thermoplastic elastomer of the comparative example 7 and the comparative example 8 which did not use this.

[0128](Example 23) The vinyl system polymer 100g which has a functional group at the end obtained in Example 11, Kneading mixing of the calcium carbonate 70g, the titanium dioxide 30g, and 0.5 g of the dibutyltin dilaurate was carried out by Plast Mill for 1 hour, and care-of-health Si and a sealing agent were produced for three days under the environment of 23 °C and 55%RH. About the obtained sealing agent, a physical-properties examination and weathering test of a normal state were done like Example 21. The test result was shown in Table 4.

[0129](Comparative example 9) It changed to the vinyl system polymer 100g which has a functional group at the end obtained in Example 11 of Example 23, and the sealing agent was produced like Example 23 except having used 100 g of polypropylene glycols of both-ends alkoxy silyl groups. About the obtained sealing agent, a physical-properties examination and weathering test of a normal state were done like Example 21. The test result was shown in Table 4.

[0130](Comparative example 10) Both-ends hydroxyl group polypropylene glycol [Mn=10000, hydroxyl value (KOHmg/g) =11.4] Carry out stoving of the 100 g at 100 °C under decompression of 5torr, and diphenylmethane diisocyanate is added so that it may be set to isocyanate group/hydroxyl group (mole ratio) =1.2 to this, It was made to react at 80 °C for 5 hours, and moisture curing type polypropylene-glycol polymer of the both-ends isocyanate group was produced.

[0131]It changed to the vinyl system polymer 100g which has a functional group at the end obtained in Example 11 of Example 23, and the sealing agent was produced like Example 23 except having used 100 g of moisture curing type polypropylene-glycol polymer of the above-mentioned both-ends isocyanate group. About the obtained sealing agent, a physical-properties examination and weathering test of a normal state were done like Example 21. The test result was shown in Table 4.

[0132]It turns out that the sealing agent using the hardenability constituent of this invention of Example 23 has the outstanding physical properties and especially outstanding weatherproof

performance of a normal state as compared with the conventional sealing agent of the comparative example 9 and the comparative example 10 which did not use these so that more clearly than Table 4.

[0133](Example 24) 100g of toluene, and silica (the product made by Japanese Aerosil.) With a homogenizer, stir "Aerosil 200" and the 30-nm mean particle diameter of 5.0 g for 1 hour, and they are distributed. After adding the toluene solution and 0.2 g of dibutyltin dilaurate of the vinyl system polymer 3.0g which have a functional group at the end obtained by this in Example 12 and also stirring for 3 hours, solid content was taken out by centrifugal separation, it washed 3 times by ethanol, vacuum drying was carried out at 80 °C for 2 hours, and refining silica was produced.

[0134]It has a flowing-back condenser tube and agitating blades, and 3.0 g of obtained refining silica was added to the 500-ml flask by which the nitrogen purge was carried out, and it was made to stir and distribute it with 50g of toluene, and 50 g of methyl methacrylate (MMA). After having added 0.1 g of azobisisobutyronitrile (azobisisobutyronitrile) to these dispersion liquid, carrying out bubbling with nitrogen gas and removing the dissolved oxygen in a system, it was made to polymerize at 60 °C for 8 hours, and silica restoration polymethylmethacrylate (PMMA) was produced.

[0135]On the PRT film by which releasing treatment was carried out, the obtained PMMA toluene solution was applied so that the thickness after desiccation might be set to 10 micrometers, and it dried for 10 minutes at 110 °C, and the silica restoration PMMA film was produced. It was 90% when the total light transmittance of the obtained silica restoration PMMA film was measured.

[0136](Comparative example 11) On the occasion of silica restoration PMMA production of Example 24, it changes to the vinyl system polymer 3.0g which has a functional group at the end obtained in Example 12, Except having produced surface treatment silica using 2.0 g of octyl trimethoxysilane, silica restoration PMMA was polymerized like Example 24, and the silica restoration PMMA film was produced. When the total light transmittance of the obtained silica restoration PMMA film was measured, as compared with the silica restoration PMMA film using the vinyl system polymer which has a functional group at 78% and the end of this invention, it was remarkable and the optical characteristic was low.

[0137]

[Effect of the Invention]The vinyl system polymer which has a functional group at the end of the invention according to claim 1, Since it is constituted as mentioned above, by the chain extension not only by reticulated-izing by bridge construction but an end functional group. Resin excellent in elongation or tensile strength is obtained, and it is used suitably for an adhesive, sealing agent, elastic adhesives, paint, foam, film, thermoplastic-elastomer, sound deadener, various molding material, and gel coat agent, artificial marble, etc. The vinyl system polymer which has a functional group at the end of this invention, It originates in the amide group which exists in the end of a polymers chain, chain extension and the reaction of hardening become certain and easy, and such reaction time is shortened, and let the workability and workability of fabrication operation or construction construction using the molding material and hardenability constituent containing these be a very good thing.

[0138]The vinyl system polymer which has a functional group at the end of the invention according to claim 2, Since it is constituted as mentioned above, the vinyl system polymer which does so the chain extension effect by the end functional group described above, and has a functional group especially in one end, Can do so the remarkable function which is not obtained with the conventional low-molecular-weight type as the resin modifier which used the functional group for the end, or a surface-active agent, and by coupling of the resin of a different presentation further. The so-called block polymer of an AB type can be compounded, and it can use effectively as a resin modifier or a compatibilizer in a similar manner.

[0139]The vinyl system polymer which has a functional group at the end of the invention according to claim 3, Since it is constituted as mentioned above, can do so the effect indicated in front 2 paragraph, and by the chain extension by an end functional group as what is called star shape polymer. The outstanding resin which the superfluous increase in crosslinking density was controlled and balance was able to take is obtained, and it is used suitably for an adhesive, sealing agent, elastic adhesives, paint, foam, film, thermoplastic-elastomer, sound deadener, various molding material, and gel coat agent, artificial marble, etc.

[0140]Since the vinyl system polymer which has a functional group at the end of the invention

according to claim 4 is constituted as mentioned above, it makes remarkable outstanding performance described above among the vinyl system polymer which has a functional group at the end of the invention according to claim 1.

[0141] Since the vinyl system polymer which has a functional group at the end of the invention according to claim 5 is constituted as mentioned above, it makes remarkable outstanding performance described above among the vinyl system polymer which has a functional group at the end of the invention according to claim 2.

[0142] Since the vinyl system polymer which has a functional group at the end of the invention according to claim 6 is constituted as mentioned above, it makes remarkable outstanding performance described above among the vinyl system polymer which has a functional group at the end of the invention according to claim 3.

[0143] Since the vinyl system polymer which has a functional group at the end of the invention according to claim 7 is constituted as mentioned above, it makes the high radical polymerization of flexibility possible, and makes remarkable outstanding performance described above among the vinyl system polymer which has a functional group at the end of the invention according to claim 1 to 6.

[0144] Since the vinyl system polymer which has a functional group at the end of the invention according to claim 8 is constituted as mentioned above, it makes the high radical polymerization of flexibility possible, and makes remarkable outstanding performance described above among the vinyl system polymer which has a functional group at the end of the invention according to claim 1 to 6.

[0145] Since the vinyl system polymer which has a functional group at the end of the invention according to claim 9 is constituted as mentioned above, it is excellent in hardening performance and makes remarkable outstanding performance described above among the vinyl system polymer which has a functional group at the end of the invention according to claim 1 to 8.

[0146] The manufacturing method of the vinyl system polymer which has a functional group at the end of the invention according to claim 10. For radical stabilization according to [] since it is constituted as mentioned above, radical dissociation of a carbon-halogen bond takes place easily, and [] to the pi electron of an aromatic ring. The chain transfer nature of the generated carbon radical is high, control of a reaction becomes easy and each vinyl system polymer which has a functional group at the end obtained shows the performance which was excellent so that it might describe above.

[0147] Since the hardenability constituent of the invention according to claim 11 is constituted as mentioned above, it shows the performance which hardened itself and was excellent in many uses described above.

[0148] Since the hardenability constituent of the invention according to claim 12 is constituted as mentioned above, it shows the performance outstanding in many uses which constitute and describe a hardenability constituent above combining a cross linking agent or a chain elongation agent.

[0149] Since the hardenability constituent of the invention according to claim 13 is constituted as mentioned above, it shows the performance outstanding in many uses which constitute and describe a hardenability constituent above combining the cross linking agent or chain elongation agent described above.

[0150] Since the hardenability constituent of the invention according to claim 14 is constituted as mentioned above, it shows the performance outstanding in many uses which constitute and describe a hardenability constituent above combining the cross linking agent or chain elongation agent described above.

[0151] Since the hardenability constituent of the invention according to claim 15 is constituted as mentioned above, it shows the performance outstanding in many uses which constitute and describe a hardenability constituent above combining the cross linking agent or chain elongation agent described above.

[0152] Since the hardenability constituent of the invention according to claim 16 is constituted as mentioned above, it shows the performance outstanding in many uses which constitute and describe a hardenability constituent above combining the cross linking agent or chain elongation agent described above.

[Translation done.]